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DETERMINATION OF THE ENVIRONMENTAL FATE OF DECONTAMINATION AGENT C-8 USING SOIL MICROCOSMS

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by

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Energy and Environmental Systems Division
Renewable Resource Section

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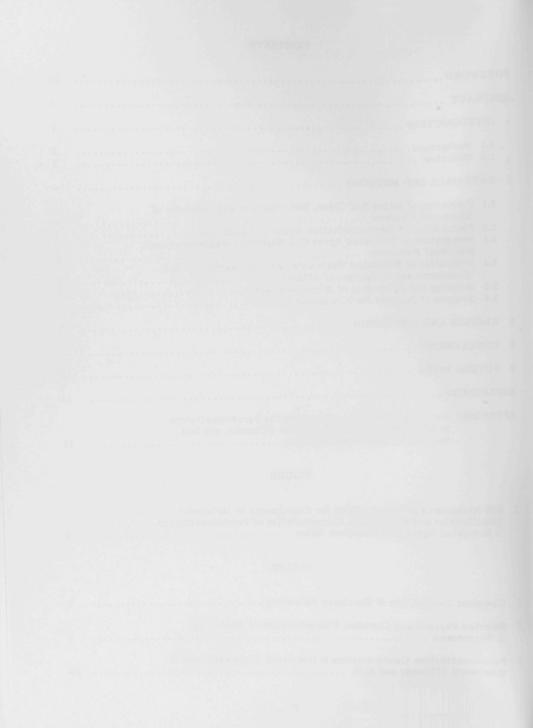
FOREWORD

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CONTENTS

FIGURE

TABLES

v

CONTENTS

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ABSTRACT

The U.S. Army is developing vehicle decontamination agents to counteract the effects of chemical, biological, and nuclear warfare agents. This study investigates decontamination agent C-8, which contains tetrachloroethylene, an EPA priority pollutant. The objective of this study was to investigate the environmental fate of tetrachloroethylene. Simulated decontamination wastewater was applied to microcosms (intact soil cores), followed by four simulated rainfall events. The wastewater effluents, simulated rain effluents, and surface soils were analyzed for tetrachloroethylene. Low concentrations of tetrachloroethylene were found only in the second rainwater effluents, but none was detected in the wastewater effluent or surface soils. The results from this study indicate that tetrachloroethylene moves through the soil more slowly than water and poses a threat of groundwater contamination because it was detected in some effluents.

1 INTRODUCTION

In the contemporary U.S. Army, integrated battlefield strategies include the use of various decontamination agents to counteract the effects of chemical, biological, and nuclear warfare agents deployed by the enemy. Because of their need to rapidly penetrate, inactivate, and remove deposits of warfare agents on vehicles and equipment, many decontamination (decon) agents contain organic or inorganic constituents that are toxic or corrosive or both. The use of decon procedures helps to ensure the protection and efficiency of troops and equipment, but it also creates the potential for soil and groundwater pollution problems if decon agents or wastes resulting from their use are accidentally released into the environment. Both federal and Army environmental regulations place considerable restraints on actual or potential generators of environmental pollution. Army regulation 200-2 requires environmental analysis and documentation for all new materials developed by research and development commands that may pollute the environment (Benford and Wentz, 1984).

1.1 BACKGROUND

Decontamination agent C-8, a new liquid decon agent planned for use primarily on tanks, armored personnel carriers, and other military vehicles, is a mixture of constituents in emulsion form. Agent C-8 contains 15% tetrachloroethylene (perchloroethylene, or PCE) and 8% calcium hypochlorite as the active ingredients. The U.S. Environmental Protection Agency (EPA) has classified PCE as a priority pollutant (40 CFR 122.53) and a Resource Conservation and Recovery Act hazardous waste (40 CFR 261.30), because PCE is a chlorinated organic solvent that is toxic to humans and animals and is a suspected carcinogen. In use, the C-8 emulsion is sprayed on the contaminated equipment and is flushed off with water after about 30 min (Department of the Army, 1983). Depending on the type of contaminant, two coats of C-8 may be sprayed on the equipment before the 30-min waiting period begins.

Accidental releases of decon agents or decon wastewater to the environment are minimized by conducting the developmental testing of decon agents over concrete sumps or other containment devices and properly disposing of the wastes. A nontoxic C-8 simulant is used for field-training exercises to prevent soil contamination. However, occasional accidents may occur in which the C-8 decon washdown wastewater may be spilled on, and infiltrate into, the soil. In these cases, it may be necessary to be able to predict the transport characteristics of various C-8 constituents in the soil, as well as the likelihood of groundwater contamination by PCE.

The nature and magnitude of environmental impacts from the accidental discharge of decon washdown wastewater into the soil ecosystem depend on many site-specific factors. Some of the more important of these factors include the concentration and volume of toxic wastewater constituents, the chemical and physical characteristics of the soil, climatic conditions (temperature, humidity, wind, etc.) at the disposal site, the amount and intensity of precipitation following the wastewater spill, and the type and amount of surface vegetation and litter. The EPA (1984) has proposed Recommended Maximum Contaminant Levels (RMCLs) of zero for PCE. The RMCLs are nonenforceable health goals that have been recommended until enforceable standards are established.

Perchloroethylene is quite volatile, but it is very persistent once in the soil (Wilson et al., 1981). Although its toxic effects on soil microorganisms are poorly known, there is some evidence that chloroethylenes can be slowly degraded by certain bacteria found in soil and groundwater (W. Mego, personal communication). However, the rates are such that biological degradation would probably have a negligible effect on wastewater moving through unsaturated soil. Agent C-8 also contains calcium hypochlorite, a source of free chlorine that could have adverse effects on potential PCE-degrading bacteria and other soil organisms in addition to the toxic effects of PCE alone. In these studies, it was assumed that removal of PCE from the soil solution as it moves through the soil profile occurs primarily through volatilization and sorption on soil solids (Wilson et al., 1981).

1.2 OVERVIEW

This report describes preliminary studies aimed at developing information and data on the environmental fate and transport of tetrachloroethylene, a chlorinated organic solvent, and other constituents of decon agent C-8 in soils. This study consists of the initial screening and ranging experiments designed to measure soil sorption (retardation) and volatilization of PCE in C-8 decon wastewater, using soil microcosms consisting of intact soil cores contained in large glass columns. The soil-microcosm experiments were planned using available data (Department of the Army, 1983) on typical decon operations. Simulated decon wastewater was infiltrated into the soil and collected after moving through the column. Four simulated rainfall events were applied to the columns, and each effluent was sampled separately. These samples, and soil samples from the columns taken after the fourth simulated rainfall event, were analyzed for PCE using gas chromatography (GC).

2 MATERIALS AND METHODS

2.1 COLLECTION OF INTACT SOIL CORES, SOIL ANALYSES, AND ASSEMBLY OF MICROCOSM COLUMNS

To provide a range of soil types for the microcosms, clay, loam, and sandy soils were identified in the local area through consultations with county extension agents and the use of county soil surveys. To realistically simulate field conditions, the soil microcosms were constructed using intact soil cores, 10.2 cm (4.0 in.) in diameter and 66 cm (26 in.) long, obtained with a hydraulic soil-coring machine. These intact soil cores have the natural horizons, structures (aggregates, pores and voids, worm holes, root channels, etc.), roots, invertebrates and soil microorganisms (bacteria, fungi, protozoans, etc.) characteristic of soils in the field. Aboveground parts of vegetation were clipped at ground level prior to coring, but the soil cores contained all belowground plant parts.

Samples representing the upper and lower halves (33 cm or 13 in.) of the core profile of each soil type were obtained from an additional core taken adjacent to the microcosm cores. These samples were analyzed for pH using standard analytical procedures (1:1 in H_2O), for organic carbon by the Walkley-Black method (Nelson and Sommers, 1982), and for texture by the hydrometer method (Day, 1965).

Each microcosm column consisted of a section of glass pipe 76.2 cm (30 in.) long with an inside diameter of 10.1 cm (4.0 in.). The soil cores were transferred directly from the coring tube to the glass columns in the field. To complete the microcosm column, a glass end cap with a Teflon® stopcock was attached to the bottom of the glass pipe section. A pad of Pyrex® glass wool at the bottom of the soil core, followed by a layer of glass beads, provided uniform support and prevented clogging of the stopcock.

Four microcosms were prepared with each soil type. Three microcosms of each soil type were used for experimental replicates and received simulated washdown wastewater. One microcosm for each soil type received only distilled water and simulated rainwater, as a control for analytical procedures. The columns were supported by wooden racks inside fume hoods in the laboratory (Fig. 1). Prior to application of the washdown wastewater (C-8 solution), the soil microcosms were flooded with water for several days and then drained to settle the soil and to ensure good contact between the soil core and the glass column wall. To avoid reactions between C-8 constituents and the test equipment, all microcosm columns, valves, fittings, collection vessels, and sampling apparatus were constructed of Pyrex® glass, Teflon®, or stainless steel. During the experiment, the temperature of the hoods and the microcosms was maintained at 22-24°C.

2.2 FORMULATION OF DECONTAMINATION AGENT C-8 EMULSION

Because agent C-8 is still under development, the complete product in emulsion form was not available and had to be formulated from constituent ingredients for this

FIGURE 1 Soil Microcosms (one set of two replicates of each soil type) Set up in a Hood for Experiments to Determine Volatilization and Retardation Characteristics of Perchloroethylene in Simulated Agent C-8 Washdown Wastewater (Teflon® effluent-sample-collection bags are connected to column stopcocks by Teflon® tubing.)

study. The description of agent C-8 that was provided (Benford and Wentz, 1984) is as follows:

> C-8 is a viscous liquid resembling heavy cream. When wet, it has the odor of dry-cleaning solvent (perchloroethylene). When dry, it has the odor of chlorine bleach. The compound is composed of 76-76.5 percent water, 15 percent perchloroethylene, 7.5-8 percent calcium hypochlorite (HTH), and 1 percent emulsifier. The emulsifier is composed of 56.5 percent calcium dodecylbenzene sulfonate, 27 percent polyoxyethylenated alcohol, 10.5 percent isopropanol, and 6 percent water. The emulsion maintains a pH of 11.1 to 11.5.

Since no specific information on formulation was available, several trial batches of agent C-8 were required in order to obtain a mixture that formed a relatively stable emulsion. An emulsion fitting the above description was obtained by using the percent by weight (wt %) of calcium hypochlorite and the percent by volume (vol %) of the liquid ingredients. The ingredients were mixed in a high-speed blender in the following sequence, blending for about one minute between ingredients: water, emulsifier, calcium hypochlorite, perchloroethylene. The resulting creamy liquid had a very strong coating action, almost like thick paint. The PCE and calcium hypochlorite used were technical-grade chemicals purchased from Fisher Scientific Co. (Chicago, Ill.). The emulsifier ("Marlowett IHF") was provided by the U.S. Army Corps of Engineers, Construction Engineering Research Laboratory (CERL).

2.3 PREPARATION OF SIMULATED AGENT C-8 WASHDOWN WASTEWATER AND SIMULATED RAINWATER

The use of agent C-8 is still under development, and it has not been used extensively in training exercises in the U.S. Therefore, some parameters have been extrapolated from data on currently used decon agents (Department of the Army, 1983).

Simulated decon washdown wastewater was produced by diluting one part C-8 emulsion with 40 parts distilled water. This dilution factor is based on descriptions of multiple-vehicle decon procedures under battle conditions at a "hasty decon site" of about 100 m^2 (120 yd^2), in which 18.9 L (5.0 gal) of decon solution (C-8) are applied to each of five vehicles and washed off with about 755 L (200 gal) of water per vehicle (Department of the Army, 1983). After standing for several minutes, the simulated wastewater (having the appearance of skim milk) separated into two phases, consisting of a cloudy translucent liquid and a whitish grease-like component that adhered tenaciously to any surface with which the wastewater was in contact.

Simulated rainwater with a pH of 4.6 and containing trace ions to mimic natural rainwater typical of the Midwest was used for the four rainfall events applied to the microcosms. The chemical composition of the simulated rainwater is presented in Table 1.

TABLE 1 Chemical Composition of Simulated Rainwater

Compound	Concentration (mg/L)
NaCl	0.176
$CaSO_4 \cdot 2H_2O$	0.709
$MgSO_4 \cdot 7H_2O$	0.355
K_2SO_4	0.069
$NaNO_3$	0.368
$(NH_4)_2SO_4$	0.746
NH_4NO_3	0.243
H_2SO_4 (96.5%)	0.987
HNO_3 (70%)	0.554

2.4 INFILTRATION OF SIMULATED WASTEWATER AND RAINWATER INTO THE SOIL MICROCOSMS AND COLLECTION OF EFFLUENTS

The total volume of decon wastewater generated for five vehicles at a hasty decon site (3879 L, or 1025 gal) was assumed to infiltrate into about 60% of the site (about 60 m^2, or 72 yd^2) with an average deposition of about 65 L/m^2 (14.3 gal/yd^2). The remaining 40% of the site (about 40 m^2, or 48 yd^2) was assumed to be either covered by the vehicle (e.g., a tank) being deconned or beyond the "splash zone" of the washdown wastewater. Based on these assumptions, an equivalent wastewater volume per unit of soil surface area of a 10.2-cm (4-in.) microcosm is 550 mL/82 cm^2. This amount of simulated wastewater was permitted to slowly infiltrate into the surface of each microcosm, with the stopcock at the bottom of the column closed. Because of the tendency of the wastewater to separate into two phases, the wastewater was strongly agitated during application to the soil columns.

The simulated wastewater was applied at a rate such that it infiltrated the soil as it was added. In all cases, the volume of wastewater was less than the total pore volume of the soil core, so there was no "head" of liquid at the top of any of the columns when all the wastewater was added. The sand and clay cores were nearly completely saturated, and the loam cores were saturated to about half of their length, by the 550 mL of wastewater added. The wastewater was allowed to remain in the microcosm for 24 h to permit maximum interaction with the soil. This condition, equivalent to temporary flooding, is not unusual under field conditions (Department of the Army, 1983). At the end of this period the stopcocks were opened, and the columns were permitted to drain for 24 h. The effluent was collected in Teflon® gas-sampling bags (Alltech Associates, Inc., Deerfield, Ill.) to minimize the loss of PCE by volatilization. The tops of the columns were open to the air at all times to simulate field conditions.

Twenty-four hours after the collection of the wastewater effluents was completed, the first of four simulated rainwater applications was made. A volume of simulated rainwater (206 mL) equivalent to 2.54 cm (1.0 in.) of rain on the soil-core surface area was applied each time and collected separately. The infiltration method, retention time, drainage time, and effluent-collection methods were as described above for the wastewater. The interval between "rains" was a minimum of 48 h. Aliquots of all column effluent samples were stored in glass vials with Teflon-lined caps prior to GC analysis for PCE.

2.5 SAMPLING AND EXTRACTION OF MICROCOSM SOILS

To determine the amount of PCE bound or remaining in the soil microcosms after rainwater leaching, soil samples were taken at 15.2-cm (6-in.) intervals along the length of the soil core immediately following the collection of the final (fourth) rainwater samples. A 2.54-cm (1-in.) diameter soil probe was pushed into the center of the soil core to the sample depth. A 1.2-cm (0.5-in.) diameter x 2.54-cm subsample was taken from the center of the 2.54-cm core to prevent contamination from intervening wet soil layers. Individual subsamples were collected from depths of 0-2.54 cm (0-1 in.), 15.2-17.8 cm (6-7 in.), 30.5-33.0 cm (12-13 in.), 45.7-48.3 cm (18-19 in.), and 61.0-63.5 cm (24-25 in.) in each soil microcosm. Three milliliters of chromatography-grade

acetone was added to the sample in an extraction vial. The soil and acetone were macerated, and the mixture was allowed to stand to permit extraction of PCE and the separation of the mixture into soil and solvent phases. After several days the acetone layer was carefully drawn off, filtered, and placed in a sample vial for GC analysis.

2.6 ANALYSIS OF SAMPLES FOR PERCHLOROETHYLENE

Simulated wastewater samples, microcosm effluent samples, and soil extracts were analyzed for PCE using gas chromatography. Details of GC column selection, calibration, preparation of standards, sample and residue extraction, sample analysis, and verification of detected constituents are presented in the Appendix, which contains descriptions of the methods used by the Organic Analysis Group, Analytical Chemistry Laboratory, Argonne National Laboratory (ANL).

3 RESULTS AND DISCUSSION

Table 2 presents the results of the soil analyses for selected physical and chemical characteristics of the three soils used in the microcosms. It should be noted that these soils represent a range of textures, as well as organic carbon content.

The C-8 decon-agent formulation trials resulted in an emulsion that remained stable for several weeks. However, when this formulation was checked after standing for about a month in a sealed container, it had separated and could not be reconstituted by vigorous shaking. The separated mixture did not have the same coating action as the original emulsion; this coating action is necessary for effective decon use. More

TABLE 2 Selected Physical and Chemical Characteristics of Soils Used in Microcosms

Soil Type and Sample Depth	pH	Carbon (%)	Sand (%)	Silt (%)	Clay (%)	Textural Class
Clay soil						
Markham-Ashkum complex,[a] Downers Grove, Ill.						
0-33 cm (0-13 in.)	7.4	6.8	41	36	23	Clay
33-66 cm (13-26 in.)	6.9	5.9	43	25	32	Clay loam
Loam soil						
Sawmill silty clay loam,[a] Indian Head Park, Ill.						
0-33 cm (0-13 in.)	7.7	2.6	39	37	24	Loam
33-66 cm (13-26 in.)	7.8	0.8	29	35	36	Clay loam
Sandy soil						
Watseka loamy fine sand,[a] Lansing, Ill.						
0-33 cm (0-13 in.)	6.5	0.9	89	8	3	Sand
33-66 cm (13-26 in.)	6.1	0.3	89	6	5	Sand

[a]Soil names from Mapes, D.R., et al., *Soil Survey of DuPage and Part of Cook Counties, Illinois*, U.S. Department of Agriculture, Soil Conservation Service, Washington, D.C. (1979).

information is needed on formulation methods for C-8 to produce a product that is stable for long periods, as would be necessary under Army distribution and use requirements.

Table 3 presents the PCE concentrations in the simulated C-8 decon washdown wastewater and in microcosm effluents and soils as determined by GC analysis. Because unanticipated sample preparation (solvent extraction of all water and soil samples) and analysis procedures [residue analysis and verification of unknowns by gas chromatography/mass spectroscopy (GC/MS) and gas chromatography/Fourier transform infrared spectroscopy (GC/FTIR)] considerably increased analytical costs, not all of the samples collected could be analyzed for PCE in this phase of the study. Several samples of the simulated wastewater applied to the microcosms were analyzed. Wastewater effluents from all three replicate microcosms for each soil type were analyzed, and rainwater effluents from at least one microcosm of each soil type were analyzed for each of the four rain events. One surface soil sample (0-2.54 cm) from each microcosm soil type was analyzed as well.

Table 3 shows that the mean concentration of PCE in samples of the simulated wastewater applied to the microcosms was 2350 ppm, which is very close to the calculated concentration of 2315 ppm. The simulated wastewater used in the microcosm transport experiments represents wastewater resulting from a "worst case" decon scenario, in which the C-8 emulsion is flushed off a vehicle without the usual 30-min waiting period, or from a case in which the undiluted emulsion is spilled on the ground and flushed directly into the soil with water.

For comparison, a wastewater sample more likely to occur in actual use was produced by swabbing the inside of a small beaker with 1 mL of C-8 emulsion, allowing it to remain exposed to the air for 30 min, and then flushing off the residue with 40 mL of water. This sample contained 64.6 ppm PCE, as compared with 2350 ppm PCE for the

TABLE 3 Perchloroethylene Concentrations in Simulated Wastewater and in Microcosm Effluents and Soils (ppm)

| Soil Surface Texture | Simulated Wastewater | Wastewater | Microcosm Effluents | | | | Effluents in Surface Soil, 0-2.54 cm[a] |
			1st Rain	2nd Rain	3rd Rain	4th Rain	
Clay	2350	0	0	0	0	0	0
Loam	2350	0	0	0.7	0	0	0
Sand	2350	0	0	6.0	0	0	0

[a]Twenty-one days after application of simulated wastewater.

wastewater used in the microcosms. The much lower PCE concentration in the "swab/wait/rinse" sample is due to PCE evaporation during the 30-min waiting period.

Table 3 shows that most of the microcosm effluents contained no PCE, although two effluents from the second rain contained small amounts of PCE (compared with the amount in the simulated wastewater). On the basis of observations made during the experiments and the results of these PCE analyses, the following interpretation explaining the loss of PCE from the microcosms is proposed. When C-8 is diluted to make the simulated wastewater, the emulsion breaks down and results in the two-phase system (milky liquid and greasy residue) described earlier. Under these conditions, the PCE concentration is higher than its solubility concentration for water (~150 ppm) and is no longer dispersed as tiny, isolated droplets as in the emulsion. Larger droplets of PCE form by coalescence and adhere to, or complex with, the calcium hypochlorite particles to form the tenacious residue that was observed. This residue adheres to various components of the microcosm soil at or near the surface, where the PCE is rapidly volatilized. When the PCE concentration in wastewater or column solutions is below its solubility concentration, the PCE behaves as a solute and is transported with the water until its movement is influenced by soil factors.

Table 3 shows that the second rainwater effluent from the loam and sandy soil both contained small amounts of PCE. It is apparent from these data that the PCE is moving through the soil profiles considerably more slowly than the water in which it was introduced. It is proposed that in these cases the PCE in solution was transported far enough into the wet soil of the microcosms so that it was not subject to rapid volatilization. It has been shown that, compared with volatilization from water, soil inhibits the volatilization of PCE and other chlorinated solvents by an order of magnitude (Wilson et al., 1981). In the microcosm, the transport velocity of the PCE was retarded by sorption to soil constituents to the extent that the PCE did not emerge until the second rainwater leach. Comparison of the velocity of water with that of PCE in the microcosms results in a retardation factor of between 2 and 3 for PCE, which agrees with a value of about 2.5 for PCE reported by Piowoni et al. (unpublished data, 1985).

It is possible that some unvolatilized PCE moved into the clay soils as well, but because of the higher clay and organic carbon content of this soil (Table 2), the transport of the PCE might have been retarded to a greater extent (Wilson et al., 1981) than in the loam or sandy soils, so that it had not emerged from the microcosm, even with the fourth rainwater leach. If this is the case, the PCE should be found in the soil samples from below the surface in the clay microcosm profile. Unfortunately, soil samples at this depth could not be analyzed in this phase of the project.

In these experiments, 10.2 cm (4 in.) of simulated rain was applied to the microcosms within a two-week period. This resulted in all of the soil profiles being in a near-saturated condition throughout the experiment. Under field conditions, this amount of rain may take from weeks to months to occur and percolate through the soil profile. In addition, the soil profile may dry to varying depths between rains, providing additional opportunity for volatile compounds (including PCE) to evaporate through open soil pores. Conversely, if a heavy storm (precipitation >2 in.) floods a site shortly after a decon operation, more PCE may be transported into or through the soil than under dry conditions.

4 CONCLUSIONS

These initial microcosm experiments indicate that even under the "worst-case" conditions, most of the PCE in simulated C-8 decon agent wastewater was lost through volatilization at or near the microcosm soil surface, because a sticky wastewater residue that contains most of the PCE adhered to, or was filtered out by, soil particles and other components near the surface of the soil. Low concentrations of PCE were detected only in the second rainwater effluent, indicating that PCE is retarded in its transport through the soil when compared to the movement of water. Only a very small fraction of the PCE present in the C-8 wastewater was detected in these rainwater effluents. Because PCE is considered a pollutant at any concentration, even these small amounts of PCE pose a threat of groundwater contamination. In most cases, actual C-8 wastewater would contain less PCE than the simulated wastewater, and actual field conditions would provide more opportunities for PCE volatilization than did the experimental conditions.

5 FUTURE WORK

As with most preliminary studies, this investigation has raised as many questions as it has answered. This study has demonstrated that it would be worthwhile to further investigate and identify key soil physical, chemical, and biological factors that control the infiltration, transport, retardation, transformation, degradation, and volatilization of the toxic constituents of decon agents. The first priority in subsequent studies should be the completion of the analysis of replicate and other samples that were taken during the current investigation but, because of funding limitations, could not be analyzed.

Soil levels of organic carbon play an important role in determining retardation factors for organic pollutants, such as PCE. A more detailed and directed study of the relationship between organic-matter content and the transport of chlorinated hydrocarbons through soil profiles could be informative and of interest to the Army.

Studies simulating actual vehicle decon procedures, including application of a decon agent and washdown, to produce a realistic wastewater simulant would be useful. Such experiments could include simulated contaminants (chemical compounds or non-infectious biological agents) to provide a reactant for the decon agent.

The role of microorganisms in soil ecology is important. Additional studies of the effects of decon constituents on microorganisms and of the possible role of such organisms in pollutant degradation are warranted. An important first step will be to determine the effect of C-8 wastewater on normal soil microorganism populations. The effects resulting from combination of PCE with calcium hypochlorite (source of chlorine) need to be determined, as well as the depth to which any such effects are significant. Soils that have been contaminated with chloroethylenes for long periods may contain adapted microorganisms that are resistant to those compounds; such microorganisms may be capable of degrading chloroethylenes more efficiently than those of uncontaminated soils.

The studies outlined above could lead to (1) the development of criteria, based on soil characteristics, for the determination of the most acceptable locations for C-8 decontamination training sites at specific Army installations; (2) the development of mitigative measures to reduce the adverse effects of C-8 on the soil environment; (3) the establishment of material handling criteria for C-8; and (4) genetic engineering studies to develop and improve soil microorganisms adapted to degrade chloroethylenes.

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APPENDIX:

DETAILED DESCRIPTION OF ANALYSIS FOR PERCHLOROETHYLENE IN DECON WASTEWATER, MICROCOSM EFFLUENTS, AND SOIL SAMPLES BY GAS CHROMATOGRAPHY*

SELECTION OF GAS-CHROMATOGRAPHY COLUMN AND OPERATING PARAMETERS

Initial work on the project consisted of establishing an analysis method for tetrachloroethylene (perchloroethylene, or PCE). This effort consisted of finding the correct gas-chromatography (GC) column, flow rate, and conditions for the analyses. The results are summarized as follows:

GC column	Quadrex 15 m x 0.32 mm MP5 (5.0-μm film)
Head pressure	14 psi
Injector	HP5880A - type B
Injection	Splitless - split 0.6 min
Initial oven temp.	100°C
Initial time	5 min
Final oven temp.	260°C
Final time	2 min
Program rate	20°C/min

Although the first column tried, 30 m x 0.32 DB5 (0.25-μm film), did not resolve PCE adequately, it was found from the relative peak widths at different starting temperatures that 100°C is the appropriate starting temperature. The second column tried provided acceptable resolution. A column velocity of 25-30 mL/min was used (14 psi). Pure (98%) PCE was well resolved from minor contaminants. It was also easily separated from potential solvents: acetone and methylene chloride. Initial work was begun by injecting the water samples neat (unextracted), first using an HP5880A GC equipped with a flame ionization detector and next with a Varian 3700 GC equipped with an electron capture detector. In both cases, the water interfered with the chromatography and made an extraction technique necessary.

Two solvents were tested for the extractions: pentane and hexane. Pentane offers the advantage of easier chromatographic separation from PCE; however, hexane is less volatile and less likely to evaporate. Methylene chloride was not tried, because it would have made future electron capture work impossible. Both hexane and pentane were tried by themselves and in combination with PCE-saturated water. The simulated wastewater sample was extracted with pentane and hexane as a final test; the hexane worked well and was chosen as the extracting medium for subsequent work.

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*Provided by J.C. Demirgian, Organic Analysis Group, Analytical Chemistry Laboratory, Argonne National Laboratory.

SAMPLE ANALYSIS METHODS

Because partition coefficients were not available, it was necessary to establish the efficiency of extraction. This was done by preparing a water solution that was saturated with PCE and extracting it with hexane. After each extraction the hexane layer was analyzed. Approximately 97% of the PCE was dissolved in the first extract. In terms of area counts, the PCE in the first extract had 4325, compared with 139 in the second extract. Hence, only a single extraction would be necessary. An extraction was then done on the sample DDC8S (run 107), and the technique worked well. After the initial method appeared successful, a PCE in hexane standard (PCESTD) was prepared and analyzed. The standard was made by weighing 66.1 mg of PCE and diluting to 10 mL (6.61 mg/ml). Two 10X dilutions were made of this stock solution [661 and 66.1 µg/mL (1000 and 100 ppm), respectively]. GC analysis showed the response to be linear throughout this concentration range. To test the accuracy of the standard, a second standard was prepared (PCESTD2), consisting of 40.8 mg PCE in 10 mL of hexane. This second standard was diluted 3X to provide a working standard of 1360 µg/mL (2060 ppm). Two 10X dilutions were made on PCESTD2 [408 and 40.8 µg/mL (618 and 61.8 ppm)]. GC runs were made on both standards to test their accuracy and precision. The data are summarized below:

Standards	Area Counts	Counts/Nanogram Injected
66.1	225	1.70 (2 ng injected)
66.1	246	1.86
661.0	2560	1.94
40.8	141	1.73
1360.0	4595	1.69

Due to the large number of samples, it is both time- and cost-efficient to develop an automated analysis program to control the autosampler, calculate the results, and store the data. An initial test on the reproducibility of the system for the 1360-µg/mL (2060-ppm) standard resulted in area counts of 6695, 6888, and 6888. Reproducibility was excellent. The retention time of PCE is 3.99 min.

It was proposed that the low results for the wastewater samples were due to the PCE adhering to the powder residue in the vials. To check this theory, the remaining 10 mL of sample was decanted from the residue and the residue extracted 2X with 2 mL of hexane. The hexane extracts were mixed with the 10 mL of decanted liquid. The hexane was removed and analyzed, and the theory was confirmed; duplicate analyses showed the residue to have significantly more PCE than the liquid.

The presence or absence of PCE in the acetone-extracted soil was not immediately apparent, because there was a major peak with a retention time of 4.45 min, approximately 0.5 min longer than that of PCE. By spiking these samples with PCE, it was determined that the unknown peak was not PCE. A GC/MS run was made, and the peak at 4.45 min was identified as diacetone alcohol. The small peak preceding it is mesityl oxide. A GC/FTIR run was made to see if there were any components that contained carbon-chlorine bonds. No halogen-containing material was found. The large

acetone solvent peak present was investigated to see if it and PCE were coeluting. By using background subtraction, it was determined that only acetone and water were present.